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Electrical properties of vacuum deposited bismuth films*

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Vacuum deposited bismuth films were investigated for their electrical behaviour between 78 to 400°K These were semiconducting and at low temperatures were *n*-type but changed to *p*-type at higher temperature The inversion temperatures, however, depended on film thickness.

1. INTRODUCTION

Transport properties of bismuth films have been studied by a number of workers with widely varying results. Earlier investigations on polycrystalline films revealed that those were semiconducting (either *n*- or *p*-type) and their nature could be changed from one type to another depending on film thickness as well as on the deposition parameters (Reimer 1957, Suhrman *et al* 1958, Fritsche *et al* 1963, Traon *et al* 1969, Bhide 1972) Duggal *et al* (1969) reported that bismuth films with the trigonal axis normal to the substrates were semiconducting due to the quantum size effect (QSE) at low thickness region less than 1000Å, whilst Hoffman *et al* (1971) found that QSE region extended to about 6000Å but the thicker films in all cases were semimetallic. All the films were, however, *p*-type irrespective of their thickness. Since the bulk bismuth is highly anisotropic in its electrical behaviour, it was felt necessary to reinvestigate in details the electrical and structural properties of the evaporated films and following is the report on them.

2 EXPERIMENTAL

Bismuth films were prepared by vacuum deposition of high purity bismuth metal (99.999% purity) at a pressure of about 10^{-5}mm Hg from a microconical silica boat heated externally by a tungsten filament which was initially flashed. The substrates used were glass slides which were cleaned in the usual way and deposition was made on them through an appropriate mask at the room temperature. These films were then annealed in vacuo at about 100°C for about an hour The depositions were also carried out in different sets keeping, however, the evaporation conditions more or less same in all cases. The length to breadth ratio of the samples was about 8.1. The film thickness was estimated by the multiple beam interferometry method. These films were also studied by the electron diffraction technique for their structural and orientation features.

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The above vacuum deposited films were then studied for their electrical property, viz., resistance (R) and Hall voltage (V_H) at different temperatures (78-400°K) for different film thicknesses (d) and parameters such as resistivity (ρ), Hall constant (R_H), mobility (μ), carrier concentration (n), etc were then evaluated using the conventional relations The details of the measuring technique and the precautions taken, etc were similar to those reported earlier (Goswami *et al* 1973). The basic arrangement consisted of a cryostat into which the sample having five leads was inserted and the whole assembly was put inside the pole gap of an electromagnet, the field and polarity of which could be varied. V_H was measured between the Hall probes, current from the potential drop across a standard resistance and resistance (R) from the potential drop between two leads and from the known current passing through the sample. Precision Vernier potentiometers (accuracy $\pm 5\mu V$) were used for potential measurements. Provisions were also made for heating and cooling these smples between the whole temperature range and chromel and p-alumel thermocouples were used for measuring temperature All measurements were carried out at vacuum $\simeq 10^{-2}$mm Hg

3 Results

(i) *Resistivity* (ρ) *and activation energy* (ΔE)

The resistance of bismuth films of different thicknesses was measured at 300°K and the resistivity was plotted as a function of thickness (figure 1). For thicker films ($d > 1000$Å) resistivity was almost independent of film thickness

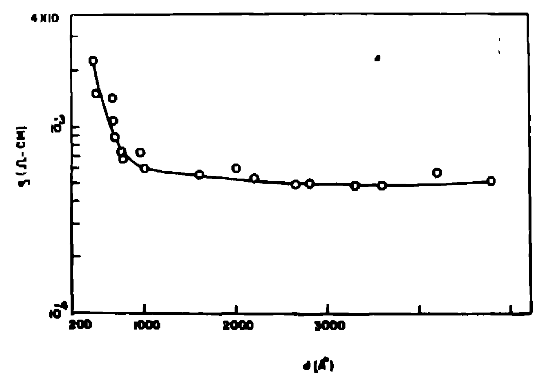

Fig 1. Resistivity *vs* thickness

but for thinner films it increased considerably with the decrease of d as is the general case of all vacuum deposits The variation of resistivity with temperature for different film thicknesses (figure 2) showed that at low temperature region resistivity was almost constant but it decreased considerably with the increase of temperature at the higher temperature region and the variation of log ρ was linear with $1/T$. This was true for all film thicknesses thus suggesting that the deposits were semiconducting in nature unlike the bulk material which is semi-metallic i e having positive TCR. Activation energy at higher temperature region estimated from the slope of the curve was about 0 05 eV

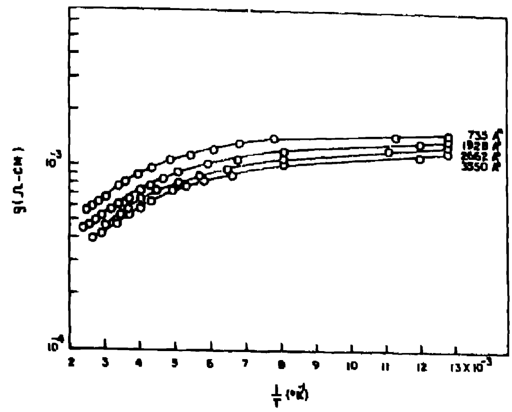

Fig 2 Resistivity *vs* 1/T

(ii) *Hall coefficient* (R_H), *carrier concentration* (n), *mobility* (μ), *etc*

Hall voltage was measured as a function of thickness at different temperatures and R_H, n, μ, etc were evaluated. Figure 3 shows a typical variation of R_H with d at two extreme ends of temperatures viz 78 and 300°K. These curves show

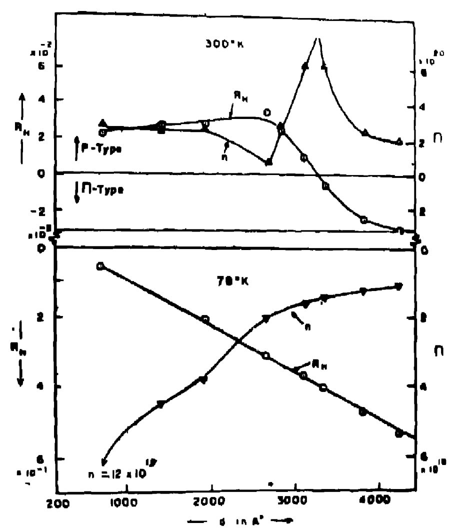

Fig. 3. Hall coefficient *vs* thickness

several features depending on the measuring temperatures It is seen that at liquid nitrogen temperature region R_H of all films ($d \approx 735$ to 4800Å) was negative and it increased almost linearly with the increasing film thickness, thus suggesting that the samples gradually became effectively purer due to the less concentration of charge carriers The estimation of n ($= 1/R_H e$) also confirms this (figure 3) It is also seen that carrier concentration of thinner films was high and almost ten times more than that of thicker films This abnormal increase in the carrier concentration is no doubt associated with the discontinuities, voids, etc. which are invariably present in the thin films.

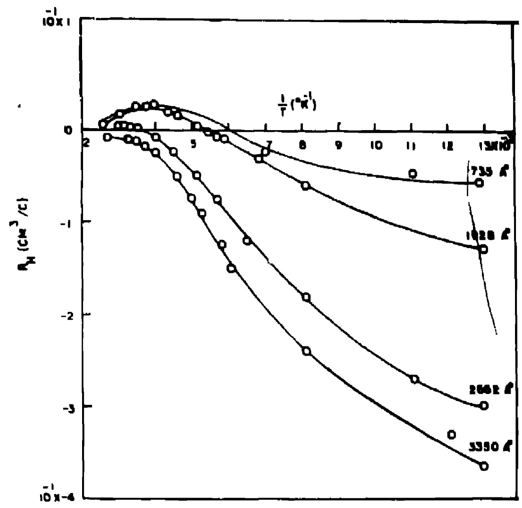

Fig. 4. Hall coefficient *vs* 1/T

R_H at 300°K on the other hand was not only positive but also showed a peak due to the predominence of holes With the further increase of film thickness it decreased and became negative, thus suggesting that the predominant charge carriers were now electrons. The effective R_H at 300°K was zero at a critical thickness of about 3200Å which, however, varied with the measuring temperature The corresponding variation of n is also shown in the graph. At the critical thickness region n cannot be calculated from R_H from the simple relation which presupposes the predominance of one type of charge carriers. The dependence of the critical thickness on the temperature at which R_H showed a change of sign is shown more clearly in figure 4 where R_H was plotted against $1/T$ for different film thicknesses It is seen that with the decrease of film thickness the transition from n-type to p-type occurred at the lower temperature region and for thinner films the critical R_H-temperature also shifted to the lower temperature region These results clearly show that the change of n- to p-type or vice versa depends not only on the film thickness but also on R_H-temperature.

Mobility also shows similar characteristics and its variation with temperature is shown in figure 5 (log—log scale). The continuous decrease of mobility, a mobility minimum, a subsequent peak in mobility graph and again its decrease with the increase of temperature except for the thick films ($d \approx 3000$ Å) are also in

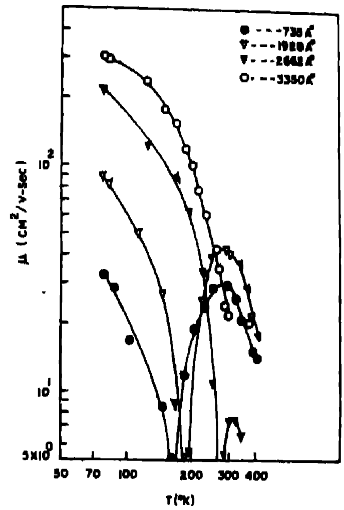

Fig. 5. Mobility *vs* 1/T

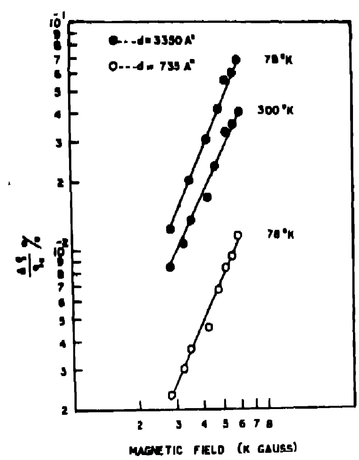

Fig. 6. Magnetoresistance *vs* magnetic field (H).

conformity with the features observed in the previous R_H graphs The mobility minimum is an indication of a critical R_H-temperature for the particular film thickness. Since for $d > 3550$ Å, R_H was always negative at all temperatures, mobility graph did not show any minimum. Thermoelectric tests at all temperatures even for thin films showed n-type behaviour.

(iii) *Magneto resistance* ($\Delta\rho/\rho$). *etc*.

It was measured with specimens having different dimensions viz. length to breadth ratio was say 1:4 instead of 8:1 adopted for Hall effect measurements. The variation of magneto resistance with magnetic field (H) at 78 and 300°K and its H^2 dependence are evident from the graph (figure 6, log-log scale).

(iv) *Structure*

A detailed electron diffraction study was also made on the surface structure of the bismuth films. These films were found to be hexagonal (rhombohedral unit cell) having the same structure as that of the bulk. These films had a textured structure and the orientation developed was mostly $1-d\{10.3\}$ type. Thicker films, however, showed better crystallinity as well as perfection of orientation (figure 7).

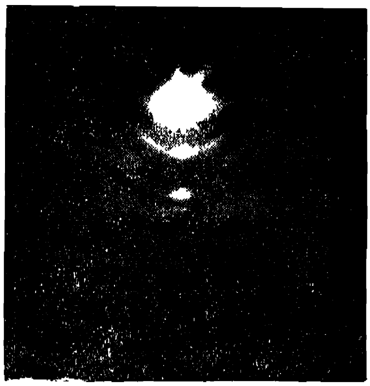

Fig. 7. $1-d\{10.1\}$ orientation of bismuth film

4. Discussions

The above study reveals that bismuth films whether thick or thin, behave more like a semiconductor as the TCR was negative unlike the bulk bismuth which is semi-metallic. The magneto resistance of these films, both at low and room temperature regions, followed H^2 law with magnetic field (1000-8000 gauss) which is also similar to other semiconducting materials. Electron diffraction studies, however, did not at all show any abnormal feature in any of these films. It therefore seems to us that the semiconducting nature of the bismuth films cannot be adduced to structures, the size of the crystallites or the preferred orientations.

The most interesting feature of the above electrical study is the thickness and temperature effects on R_H, n and also on μ. It is wellknown that vacuum deposited thin films are discontinuous in nature and contain many voids in addition to innumerable imperfections such as dislocations, grain boundaries, misfits of atoms, misalignment of crystallites, stress, etc. With appropriate annealing in vacuo these defects can only be partially removed. In any semiconducting material, these would create impurity centres in the energy band gap even though starting material was highly pure. With increasing thickness some of these defects,

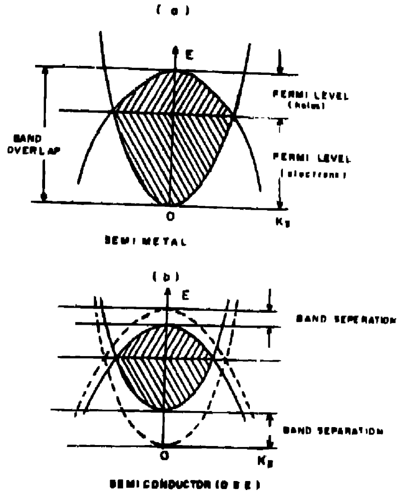

Fig. 8 Band structures for bulk and semiconducting bismuth

namely, voids, discontinuity, etc will at least partially be removed thus decreasing the effective defect concentration hence also the carrier concentration. Such film will also show a comparatively lower resistivity as observed in the present case (figure 1). The decrease of the effective carrier concentration is clearly seen in figure 1 (78°K) where R_H continually increased and n decreased with increasing film thickness In fact, the carrier concentration of thinnest films ($d = 735$Å) was about 10 times more than the thicker films. Further the negative R_H for all films at low temperature region really indicate that the majority charge carriers were predominently electrons. However, the variation of R_H and the reversal of the sign with increasing temperature suggest that the current carriers in this films were both electrons and holes Presuming a mixed type of conduction at least around the transition temperature R_H is given by the relation

$$R_H = \frac{1}{e} \frac{n_p\mu_p^2 - n_e\mu_e^2}{(n_p\mu_p + n_e\mu_e)^2}$$

Since R_H was negative in the lower temperature region, then $n_e\mu_e^2 > n_p\mu_p^2$ But with the increase of temperature R_H however decreased, and at transition temperature $R_H = 0$, hence $n_e\mu_e^2 \approx n_p\mu_p^2$. When R_H changed its sign and became positive at the higher temperature region it suggests that the effect of holes become predominant. Thus these observations of ours are in agreement with the observations made by previous workers who observed that the bismuth film could both be n-type and p-type (loc. cit). It is not yet clear to us why this change of n to p-type depending on d and temperature occurred for these films. This may be associated with surface states caused by the presence of residual gas molecules thus creating p-sites by absorption of gases etc even though the film may be n-type Since the effect is more prominent for thinner films, the above assumption is reasonable. The thermoelectric tests did not show the above effects. As the tests are only indicative it may not be sufficiently sensitive to this process

The semiconducting behaviour of semi-metallic bismuth in thin film state may arise from one of the following causes :

(a) The presence of potential barriers in the discontinuous films having island structures where conduction under an electrical field can take place by direct tunnelling or through substrate as proposed by Minn (1960), Neugebauer *et al* (1962).

(b) The quantum size effects (QSE) where the film thickness is comparable to the de Broglie waves (Ogrin *et al* 1966, Sandomirskii 1967) The theoretical treatment for such a case has been given by Sandomirskii (1967)

The former mechanism, however, presumes an island structure and discontinuity of these films. In the present case since the semiconducting behaviour was observed even for very thick films ($d \approx 3550$Å) where island structures will no longer be present, it seems that the former mechanism may not be valid for inducing semiconducting properties Due to QSE the overlapping of conduction and valence bands valid for the semi-metallic state split into sub-bands with the decrease of film thickness. If the thickness is substantially small, small gaps are reformed and a semi-metal becomes a semiconductor (figure 8 after Sandomirskii 1967) This effect is important because of its dependence on film thickness and hence it can change from the degenerate state to non-degenerate one Since the limit of QSE as observed by Hoffman *et al* (loc. cit) is quite high it seems to us that the above band structure explains reasonably the electrical behaviour of bismuth films.

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